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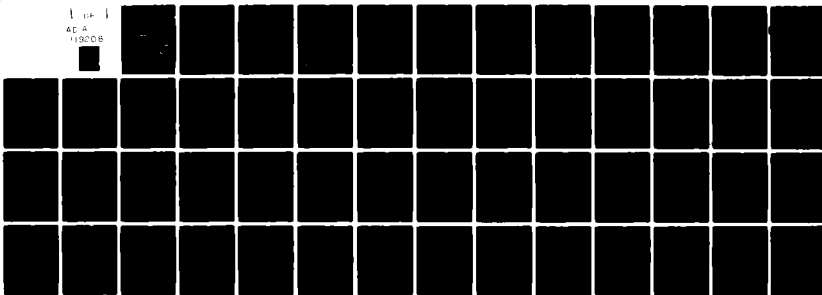   MAY 82 M LAVID   F49620-81-C-0028
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RADIATION/CATALYTIC AUGMENTED COMBUSTION

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MOSHE LAVID
CORPORATE RESEARCH-TECHNOLOGY FEASIBILITY CENTER
EXXON RESEARCH AND ENGINEERING COMPANY
LINDEN, NEW JERSEY 07036

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MAY 1982

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Two novel concepts for extending aircraft operational range have been researched under this contract. They are radiative and catalytic augmentation techniques. The objective is to investigate the feasibility of the techniques to enhance combustion initiation and reaction kinetics which restrict combustion operation via limits on flammability, flame propagation, ignition and stability. Both techniques have demonstrated the potential to enhance combustion processes and to broaden normally encountered stability limits. The radiative technique under

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static conditions has successfully ignited fuel-air mixtures, and has enhanced combustion processes, utilizing pulsed and continuous VUV light sources. Similarly, the catalytic technique has provided efficient combustion under normally difficult fuel lean, low temperature, conditions. A complementary effort has focused on the development of analytical capabilities required for modeling the radiative and catalytic techniques.

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FOREWORD

This is the first annual report on research in Radiation/
Catalytic Augmented Combustion conducted with partial support of the
Air Force Office of Scientific Research under Contract No. F49620-81-
C-0028, with Dr. B. T. Wolfson as the AFOSR Program Manager. This
research under the new contract succeeds and continues the work performed
under previous Contract No. F49620-77-C-0085, and described by Final
Technical Report (AFOSR-TR-82-0132).

This first annual report covers the progress of research over
the last 12 months; since its inception on April 1, 1981 thru March 31,
1982. The work was performed at Exxon Research and Engineering Company,
Linden, New Jersey with Dr. M. Lavid as the Principal Investigator. With-
in Exxon, the work was carried out in the Corporate Research-Technology
Feasibility Center, System Advancement and Transfer Laboratory.

ABSTRACT

Two novel concepts for extending aircraft operational range have been researched under this contract. They are radiative and catalytic augmentation techniques. The objective is to investigate the feasibility of these techniques to enhance combustion initiation and reaction kinetics which restrict combustor operation via limits on flammability, flame propagation, ignition and stability. Both techniques have demonstrated the potential to enhance combustion processes and to broaden normally encountered stability limits. The radiative technique under laboratory static conditions has successfully ignited fuel-air mixtures, and has enhanced combustion processes, utilizing pulsed and continuous VUV light sources. Similarly, the catalytic technique has provided efficient combustion under normally difficult fuel lean, low temperature, conditions. A complementary effort has focused on the development of analytical capabilities required for modeling the radiative and catalytic techniques.

The radiation technique utilizes selected wavelengths in the vacuum ultraviolet region to photodissociate molecular oxygen into oxygen atoms. When a critical concentration of atomic oxygen is achieved (about 10^{16} atoms/cm^3), combustion initiation occurs. Subsequent reactions of the atomic oxygen with fuel molecules, as well as with other combustion species, lead to ignition and sustained combustion via chain reactions. All radiative ignition and combustion enhancement tests under various static conditions were completed. They included new VUV excimer laser ignition tests, and additional ignition and enhancement experiments employing a continuous light source (EIMAC). The primary accomplishment of the laser work was the demonstration of the important role of the spectral selectivity of the absorption coefficient of molecular oxygen in the initiation process,

The VUV output of the continuous light source was found to be marginal for ignition as well as for enhancement. Nevertheless, it successfully ignited a propane/O_2 mixture for the second time. Furthermore, it was used to obtain more combustion enhancement results which seemed to be supportive of the radiative concept.

The catalytic combustion is a concept wherein combustion reactions initiated by a heterogeneous catalyst play an important role in the energy release process of a reacting fuel-air system. This program is primarily aimed at improving flame stabilization and reducing pressure loss in aircraft afterburner systems. It proposed to replace the conventional bluff-body by a catalytic flameholder in an attempt to extend further the stability limits. The bluff-body stabilizes the combustion by forming a recirculation zone which, in turn, enhances mixing and heat transfer. However, it also causes a substantial pressure loss. The key role of the catalyst is to "bootstrap" the conditions of temperature and concentration of reactive species to levels favorable for stable and efficient combustion. The suggested advantages of the catalytic flameholder over the bluff-body are: (1) reducing the pressure loss and (2) providing more stable combustion due to its porous structure and its thermal inertia, respectively. To this end, a Plug Flow Combustor has been constructed for conducting tests to determine the stability limits and the pressure loss of premixed propane-air flames behind a bluff body and behind a catalytic monolith of equal cross-sectional area.

STATEMENT OF WORK

The work statement covering the contract period 1 April 1981 thru 31 December 1982 is presented below. A program timetable chart is provided in Figure 1:

The contractor shall furnish scientific effort during the funding period, together with all related services, facilities, supplies and materials, needed to conduct the following research. The professional manpower level for this Work Statement is 2365 man-hours.

I. Radiative Augmentation

   1. Static Experiments

      a. Continue radiative static combustion experiments. Use pulsed ILC and continuous EIMAC light sources to determine and measure photochemical ignition and combustion enhancement.

      b. Select and employ appropriate vacuum ultraviolet lasers to conduct radiative static experiments. Investigate the dependence of radiative ignition and enhancements on light wavelength. Identify the most effective wavelength width(s) for augmentation applications.

   2. Flow Experiments

      c. Provide a combustion test facility to conduct radiative and catalytic experiments under flow conditions. Use advanced diagnostics where necessary to obtain high quality experimental data.

      d. Design and conduct radiative experiments under flow conditions. Investigate radiative effects on ignition and combustion enhancement in premixed flowing reactive mixtures subjected to pulsed or continuous vacuum ultraviolet light. The objective is to attempt to demonstrate radiative augmentation under flow conditions.

3. Analytical Modeling

e. Incorporate the emission characteristics of the light sources used into the current combustion initiation model. Compare the experimental data with the model results. Use the model to elucidate the photoabsorption-kinetics interaction and to assist in system optimization. Include heat loss mechanism, species diffusion and wall recombination in the model. Undertake additional model revisions and refinements as deemed necessary.

4. Evaluation

f. Analyze and assess the experimental and analytical results, particularly as they apply to application in practical combustion hardware.

g. Develop a test plan for larger scale combustion tests of the most promising radiative augmentation technique(s).

II. Catalytic Augmentation

1. Design and Acquisition

h. Design, fabricate, and/or acquire catalytic flameholders. Evaluate and screen chemical and physical characteristics of flameholders to determine best candidates for flow experiments.

2. Flow Experiments

i. Perform experimental flame stabilization tests on a standard V-gutter, and non-catalytic and catalytic monoliths under both non-reacting and reacting flow conditions.

j. Perform experimental flame stabilization test on best flameholder candidates determined in Work Statement #h.

3. Analytical Modeling

k. Review and revise existing catalytic flameholding model
to obtain a sufficiently detailed, balanced engineering model. Compare
model predictions to experimental data to ascertain agreement and resolve
any discrepancies in regimes of interest. Use the model to explore
the interaction of aerodynamic effects and catalytic and homogeneous
combustion. Utilize the model, as an adjunct to the experimental effort
in initially analyzing the data and ultimately in performance optimization.

4. Evaluation

l. Analyze and assess the experimental and analytical results,
particularly as they apply to application in practical combustion hard-
ware.

m. Develop a test plan for larger scale combustion tests of
the most promising catalytic augmentation technique(s).

Program Timetable

The Work Statement for this contract covers the period April
1981 thru December 1982 and is summarized in the preceding section.
Figure 1 provides the timetable chart for this work. As anticipated,
the radiative static experiments, as well as the initial design of the
catalytic flameholder, were completed by the end of the third quarter
of 1981. However, the flow experiments did not commence until the
second quarter of 1982, because of an unexpected delay in the construc-
tion of the combustion test facility. Therefore, the flow experiments
will proceed until the end of the contract. The Analytical Modeling and
Evaluation have been considered as continuing tasks throughout the pro-
gram. This has provided the means for maintaining close interaction
among the various tasks and especially has ascertained interaction be-
tween experimental results and theoretical data. Technical Reports and
oral presentations have been provided on an annual and a semi-annual basis,
respectively, as indicated in Figure 1.

Figure 1. Program Timetable Revised (3/16/81)

CY		1981									1982										1983		
FY		FY 80/81						FY 81/82											FY 82/83				
Mos.		4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3

I. Radiative

1. Static expts.
   ILC & EIMAC   1 Pro man/month (m/m)
   VUV laser   1 m/m

2. Flow expts.   4 m/m

3. Analytical Modeling   2 m/m

4. Evaluation/Documentation   1 m/m

II. Catalytic

1. Design, acquisition & screening   1 m/m

2. Flow expts.   4 m/m

3. Analytical Modeling   2 m/m

4. Evaluation/Documentation   1 m/m

▲ Report

● Presentation

STATUS OF RESEARCH EFFORT

This section describes the program research accomplishments since its inception on April 1, 1981, and covers the work performed through March 31, 1982.

All the radiative static experiments were completed. They included new VUV laser ignition tests, additional continuous light source (EIMAC) ignition tests, and a considerable amount of enhancement tests. The VUV laser ignition work was conducted by employing an excimer laser at two VUV wavelengths 157 nm (F_2) and 193 nm (ArF). Radiative ignitions were achieved with the fluorine laser and not with the argon fluoride laser, even though the latter has about 20 fold greater fluence. This result demonstrates the important role of the spectral selectivity of the absorption coefficient of molecular oxygen. Successful radiative ignitions with a continuous light source (EIMAC) were found to be reproducible only after many attempts due to the marginal VUV output of this xenon lamp. Although its VUV output is marginal it is currently the best continuous VUV light source and therefore it was used also in the combustion enhancement work. A large number of tests investigating propane-air flames were conducted. Due to experimental difficulties and the marginal VUV output, the data obtained were limited and not conclusive. Nevertheless, the results seemed to be supportive, though not quite confirmative of the radiative enhancement concept.

In a complementary analytical effort, a radiation initiation model has demonstrated good phenomenological agreement with the observed ignition behavior; particularly, it has shown good quantitative agreement with the laser ignition results attesting to the adequacy of the model for elucidation of photon-radicals interaction in combustion initiation. A quite different numerical model, developed at Lawrence Livermore Lab., has been used to examine the enhancement results obtained in a propane-air flame.

The model consists of a one-dimensional, time-dependent treatment of the conservation equations, together with detailed chemical kinetic mechanism including photodissociation reactions. Only limited combustion conditions were simulated by this model because of the edit facilities of the computer program. It was found that the amount of data output was unusually large making direct comparison with the experimental results very difficult. A reduction of the numerical output to manageable quantities seemed desirable.

The research effort in the catalytic augmented combustion part of the contract focused on the completion of the test facility. A Plug Flow Combustor (PFC) was constructed to conduct experiments under flow conditions. It is a highly flexible device which can be used to study combustion up to high gas velocities encountered, in particular, in gas turbine engines. It was designed with optical ports to make it compatible with advanced laser diagnostics, and to allow the use of VUV laser. Although this new combustor permits the study of both radiative and catalytic augmented combustion, it is intended to be used primarily for the catalytic work. This work has been revised to conduct flame stabilization tests under realistic conditions of sustained combustion in flowing system. The main objective is to determine whether the stability limits achieved with a standard bluff body can be further extended by replacing it with a catalytic monolith of equal cross-sectional area, and whether the pressure loss associated with the bluff body can be reduced by using its catalytic surrogate. The standard bluff bodies, the non-catalytic and the catalytic monoliths have been acquired and flame stabilization tests are ready to start.

The completed radiative augmented combustion work under static conditions is described below.

Radiative Augmented Combustion

1. Static Experiments

The radiative augmented combustion work under static conditions was completed. The experimental apparatus was described in detail elsewhere[1] It consists of a quartz cylindrical combustor chamber, 2.5 cm diameter and 30 cm long that can be irradiated end-on by light sources of various types. This configuration provides the capability of studying the interaction of vacuum ultraviolet (VUV) and ultraviolet (UV) radiation with gaseous fuel-air and fuel-oxygen mixtures at subatmospheric and atmospheric pressures and at room temperature.

The static experiments have been divided into two subjects: ignition and enhancement. Combustion ignition is achieved by using either a light source or in-situ spark discharges, or a combination of both. The light source is fixed on the left-hand side of the combustion tube while the spark electrodes can be discharged on either side of the tube resulting in a flame propagating into or away from the light source. Ignition has been attempted by using pulsed and continuous VUV and UV radiation from various xenon lamps and excimer lasers. Combustion enhancement has been investigated using a continuous light source (EIMAC).

Ignition: Various gaseous fuel/air and fuel/oxygen mixtures have been successfully ignited by using appropriate light sources (no thermal effects). Extensive radiative ignition tests, using ILC pulsed light sources, were conducted under static conditions. Successful ignitions were obtained and minimum ignition energies were determined for various equivalence ratios at atmospheric and subatmospheric pressures[1]. A few of the reactive mixtures ignited by the pulsed ILC light source were hydrogen/oxygen, methane/air and propane/air. In all of these tests, the spectral distribution

of intensity of the light sources was not accurately known. Based mostly on manufacturers' data and to some extent on our spectrographic diagnostic tests, it was assumed that the ILC pulsed light source has a spectral range of 140 to 200 nm, while the EIMAC continuous light source has a broader range of 150 to 400 nm. Furthermore, it was assumed that the power output in the UV range was less than 2% of the total output. For example, in the case of the EIMAC lamp out of 500 W output only 4 to 10 watts are believed to be in the UV range. With the current rapid development in laser technology it has become possible to use excimer lasers instead of xenon lamps as VUV light sources for radiative tests. Since laser light is emitted at discrete and very narrow wavelength band, it is considered as a superior research tool to any lamp, in investigating the effect of light wavelength on combustion augmentation. Two excimer laser were identified; the Lumonics TE-861 and the Lambda Physik EMG-200, and the former was employed in the new laser ignition tests.

The laser ignition experiments were conducted at Los Alamos Scientific Lab/Applied Photochemistry Division using their Lumonics TE 861 laser facility. The main objective of these experiments was to investigate the effects of light wavelength and fluence on radiative ignition, which, in turn, will assist us in better understanding the role of photodissociation reactions in the entire kinetic scheme. For this reason we selected hydrogen with air and hydrogen with oxygen as the combustible mixtures. The kinetics of which are well known and documented in the literature. The lasers used were at two wavelengths; 193 nm (ArF) and 157 nm (F_2) with a measured fluence of about 300 to 400 and 20 to 40 mJ/cm^2, respectively. The experimental variables were the equivalence ratio, the pressure, the optical path, the fluence and the location of the focal point.

Tests began using the ArF laser, although theoretical calculations performed prior to conducting these tests (See Section; Analytical Modeling) predicted no radiative ignition with the ArF laser with either H_2/air or H_2/O_2 mixtures (ϕ = .6 to 1.6), unless its fluence can be increased by several order of magnitudes from the currently available level. Contradictory to our numerical predictions, we surprisingly obtained ignitions with the ArF laser. These laser ignitions were first obtained with H_2/air mixtures at equivalence ratio of unity, at atmospheric pressure of 585 mm Hg (Los Alamos is at elevation of 7,000 feet), optical path filled with air or with argon, fluence of about 350 mJ/cm^2, and with the focal point at the inner side of the window. Since it was quite difficult to reproduce these marginal laser ignitions we decided to change the equivalence ratio from the stoichiometric value to fuel lean (ϕ = .65), which theoretically is more favorable for radiative ignition. At this new fuel lean conditions we obtained reproducible laser ignitions at subatmospheric and atmospheric pressures. Most surprisingly, laser ignitions were also obtained when we changed the gases in the optical paths from argon to air and to oxygen. These results immediately arose suspicions concerning spark (thermal) ignitions rather than the unexpected radiative ignitions, because air and oxygen strongly absorb the light at this wavelength. We carefully examined the laser beam at the focal point and revealed that it, indeed, caused the sapphire window and sometimes the flange (at i's inner diameter) to spark depending on the location of the laser beam.

In an attempt to avoid laser induced sparks we tried to reduce the fluence and also to move the focal point into the combustor chamber until no spark was visible. After doing that we still obtained ignitions with Ar as well as O_2 optical paths. The consistent successful ignitions

especially with the oxygen optical path indicated to us that the ignitions are not radiative and are probably thermal although we could not detect any sparks.

At that stage we decided to change the mixture from H_2/air to fuel lean H_2/O_2 which is most favorable for radiative ignition. This allowed us to reduce further the fluence in an effort to eliminate laser induced sparks. We set the equivalence ratio at .613 and the pressure at 100 torr. We conducted 10 tests with optical path of argon and 3 tests with optical path of oxygen. Regardless of the optical path, all tests ignited suggested thermal rather than radiative ignitions as explained above. This is true although the sparks were not always visible.

Based on the ArF results we concluded that ignitions obtained with this laser are thermal and not photochemical. The ArF laser has apparently adequate fluence to cause the window or the supporting flange to spark. This conclusion is corroborated by the fact that the required minimum energy for spark ignitions in these mixtures is between 2 to 10 mJ, and the measured laser pulse energy is more than 50 mJ, which is in excess of the minimum energy required for thermal ignition.

The laser ignition tests were resumed with the F_2 laser. This laser was considered more suitable of achieving radiative ignitions for two reasons. The first reason is that with this laser the system is less susceptible to laser induced sparks because the F_2 pulse energy is only 12 mJ, which is considerably lower than that of the ArF, 50-200 mJ. The second reason lies with the strongly wavelength-dependent absorption coefficient of molecular oxygen. It sharply increases (four orders of magnitude) as the wavelength decreases from 193 nm (ArF) to 157 nm (F_2). Thus, although the fluence of the F_2 laser is about 20 fold smaller than that of ArF laser, it is remarkedly more efficient in producing atomic oxygen.

As in the case of the argon-fluoride laser, we began the fluorine laser tests with numerical calculations, using our radiative initiation model. The numerical results predicted that the F_2 laser is capable of achieving radiative ignitions, and revealed that ease of ignition is increased with an increase in pressure as well as in fluence. Moreover, they showed that it is easier to ignite H_2/O_2 mixture than H_2/air mixtures, and that fuel-lean mixtures are more favorable for radiative ignitions than fuel-rich mixtures.

With this theoretical knowledge the tests were begun. It was found, indeed, that the F_2 laser is very capable of radiative ignitions. However, the first successful ignition was not obtained until after a very thorough investigation of the F_2 laser characteristics.

It was found that:

(1) The laser power is rapidly decreased with time (number of pulses) as depicted in Figure 2, and thus the F_2-He mixture in the laser chamber has to be exchanged very frequently (approx. 10 mins, 800 pulses).

(2) The maximum pulse energy of the F_2 laser reported by the manufacturer (Lumonics) is 10-12 mJ. This is the total energy, and it consists of visible (red) energy and invisible (VUV) energy. The red energy is probably emitted by the fluorine atoms while the VUV radiation is emitted by the excited F_2 molecule. The net VUV energy is only 4-6 mJ rather than the reported 10-12 mJ. Examining Figure 2 reveals that the net VUV energy decreases with time while the red light energy is constant.

(3) It seems that the total pulse energy is not sensitive to the voltage across the laser electrodes. It reaches a

Pulse Energy (No Transmittance Loss) Vs Time (Number of Pulses)

Figure 2

Legend:

| + | Total energy (He purge) |
| o | No VUV (air purge) |
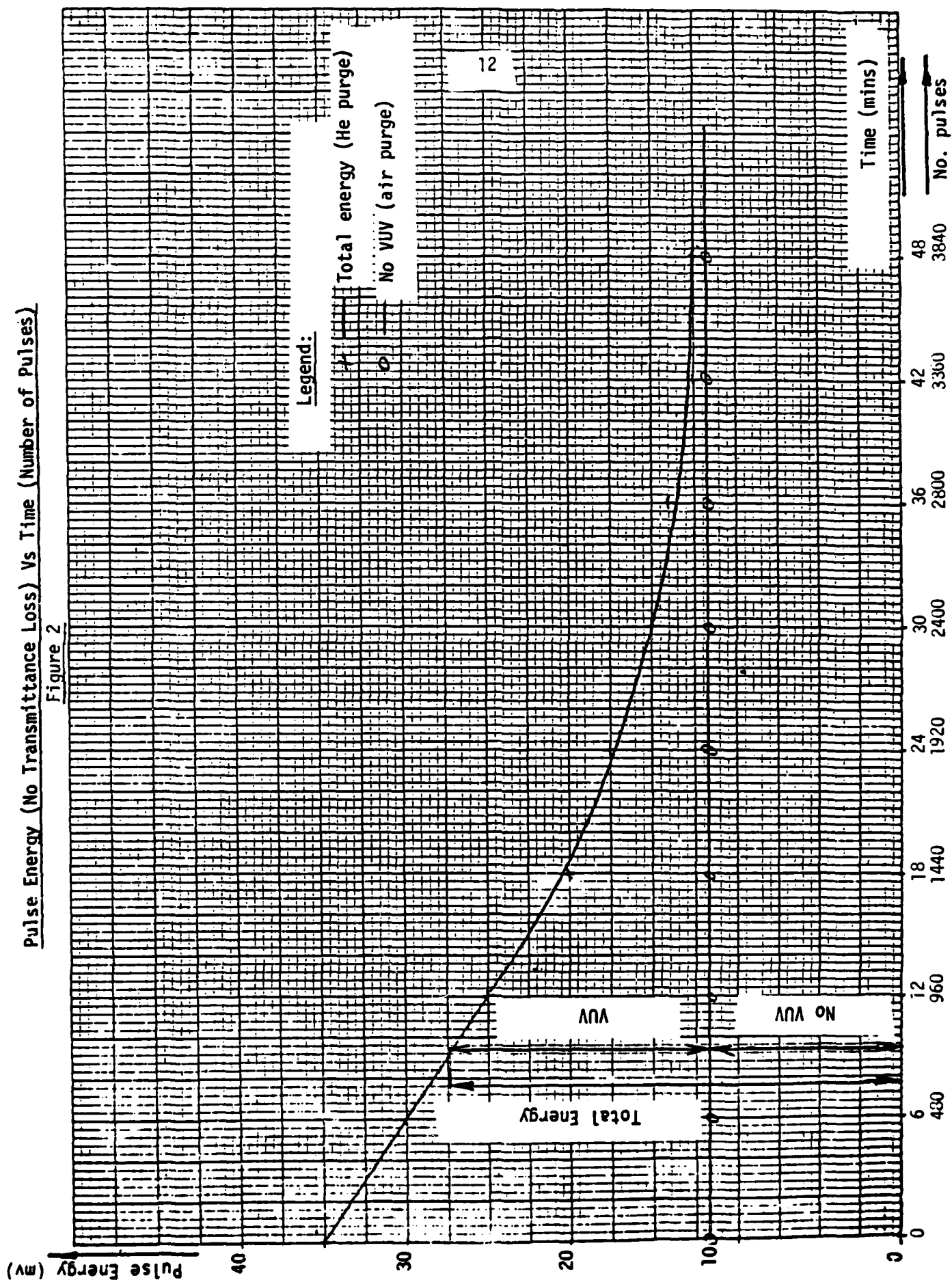
steady state value of about 8 mJ at a voltage range of 27-31 kv. Thus, during all our combustion experiments the laser voltage was set at 29-30 kv. This finding was somewhat unexpected.

(4) In the optical path between the laser and the reactive mixtures we had a pl/cx LiF lens with a focal length of 200 nm, and a MgF_2 window 2 mm in thickness. Although these materials are considered to be among the best VUV transmitters, each of these optical components suffered a loss of about 50%. Thus, the net VUV pulse energy reaching the combustible mixture was only 25% of the total VUV energy emitted by the laser. The average measured VUV fluence available for combustion was only 30 mJ/cm^2. After a few minutes these values decreased even further, as explained in (1).

(5) A very important finding was the exact location of the VUV focal point. The experimental results are depicted in Figure 3. The abcissa is the distance between the inner side of the MgF_2 window and the LiF lens. The ordinate is the maximum energy incident on a photodetector with an iris of ϕ 1 mm. The data represented by the solid line was taken with He purging the optical path and thus it is total energy (VUV + red). The dashed line represents energy without VUV, since the optical path was purged with oxygen. The difference between the two curves is net VUV energy. Examining the curves clearly reveals that the VUV focal length is 19.5 cm. The other focal length at a distance of 22.5 cm is for the visible light and it is not adequate for VUV. The two focal points are apart by about 3 cm. This finding was corroborated by calculating the effect of the refractive index on the focal length. The VUV

Figure 3

Pulse Energy (With Lens and Window Losses) Vs Distance
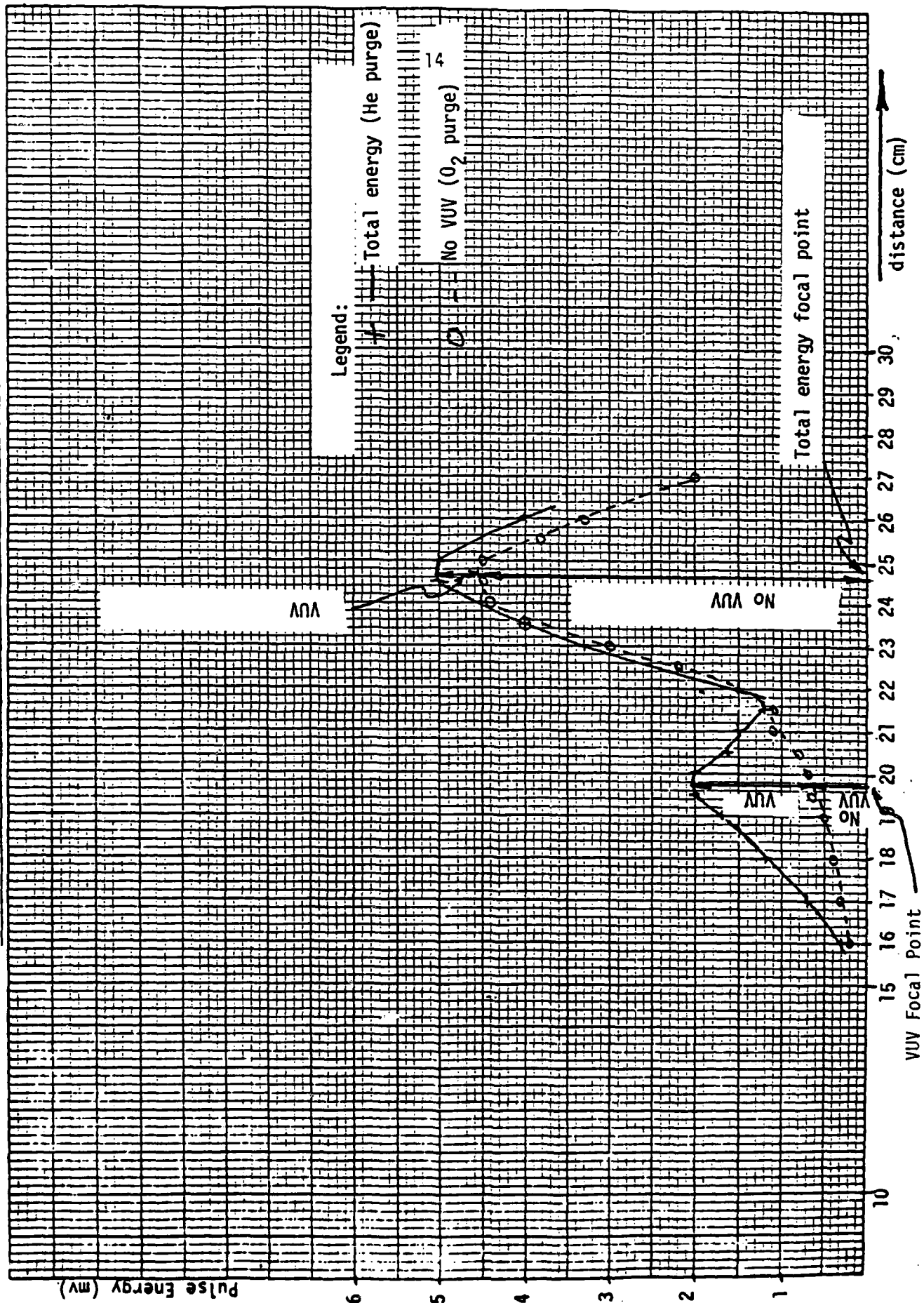
refractive index in LiF is higher than that of the red light

resulting in a shorter focal length by about 3 cm.

(6) Once the focal point was adjusted and set for maximum VUV

pulse energy, ignitions were easily obtained. For example,

with H_2/air mixtures ignitions were obtained for a range of

equivalence ratios of .34 to 1.50 at subatmospheric pressures

with VUV energy of approximately 0.1 to 0.3 mJ. In comparison,

reported[2] range of minimum spark ignition energy for H_2/air

at comparable equivalence ratio but at atmospheric pressure is

.02 to .03 mJ. However, higher minimum spark ignition energies

of 2 to 10 mJ were previously measured in our laboratory.

(7) Unlike the ignitions obtained with the ArF laser which were

caused by laser induced sparks, those obtained with the F_2

laser were radiative ignitions. This was confirmed by conducting

two independent tests. In the first test, after obtaining

radiative ignition at a focal point setting of 19.5 cm, the

lens was moved to the second focal point (22.5 cm). Although

the total amount of energy at the longer focal is much greater

than that at the shorter focal point, no ignition was obtained

at a distance of 22.5 cm. In the second test, the focal point

was kept at 19.5 cm, but the optical path was purged with oxygen.

No ignition was obtained with oxygen purging, but as soon as Ar

or He purging replaced the oxygen, ignition occurred. In

addition, the window was carefully examined and no visible or

audible signs of sparks were found. This is also supported

by the fact that the F_2 laser flux is about 10^6 to 10^7 W/cm^2,

and the optical breakdown is generally caused at higher flux[3]

of 10^9-10^{10} W/cm^2.

In summary, the laser ignition experiments confirmed the radiative ignition concept. They showed that the F_2 laser is very capable of achieving radiative ignitions and that it is probably the best available VUV source for conducting future radiative combustion tests. Furthermore, the results obtained with the ArF and the F_2 lasers were in very good agreement with our numerical predictions, as described in a subsequent section - Analytical Modeling. This agreement strengthens our confidence in the correctness of the radiative ignition model, which may be extended to account also for combustion enhancement.

The first successful radiation ignition with a continuous light source was reported in the Third Interim Report[4] of the previous contract. The EIMAC continuous light source ignited a stoichiometric mixture of gaseous propane-oxygen at atmospheric pressure and room temperature. Indeed, the radiative ignition caused a detonation wave which shattered the quartz reactor and cracked the lamp. A new lamp was ordered and a considerable effort was made to reproduce this result, but not before the completion of the static enhancement work for which the same lamp was needed. In an attempt to protect the lamp from the detonation wave, the first set of experiments was conducted at subatmospheric pressures, incrementally increased from 50 up to 400 torr. No ignition occurred for stoichiometric propane-oxygen mixtures. In the second set of experiments, these tests were repeated with an increase of 23% in the lamp power output. The maximum power recommended by the manufacturer is 500 W. The power used in the second set of tests was 615 W. These tests also resulted no ignition. In the third set of experiments the equivalence ratio was changed from 1.0 to 0.80 and, the pressure was allowed to increase up to 1 atm. Again, no ignition was obtained. In the last set of experiments, everything was maintained constant with the exception of the lamp location.

The lamp was moved horizontally such that its focal point traveled near the inner edge of the window in increments of 0.1 mm. Finally, ignition occurred. The combustion tube exploded and the lamp cracked. This second successful ignition happened at equivalence ratio of 0.8, power output of 615 watt and pressure of 1 atm. The first reported ignition happened at slightly different conditions; equivalence ratio of 1.0, and power output of 500 watt (however, a different lamp). It is believed that the VUV output of the lamp is very marginal for radiative ignition. This explains why a successful ignition was obtained only after the focal point and the inner edge of the window were brought into close alignment, maximizing the amount of VUV radiation available at the inlet of the combustor.

It is believed that the detonation waves resulted from these two successful ignition tests are similar to those reported by Lee et al.[5], which required a minimum value of photodissociative free radicals as well as an adequate gradient of these radicals. These reproducible radiative ignitions with continuous light source imply the potential for using the light as an optical flame stabilizer with no pressure loss instead of the conventional intrusive flameholders which cause a pressure drop of up to 10%.

Combustion Enhancement: Combustion enhancement experiments have been conducted with propane/air mixtures at various equivalence ratios and pressures. The average flame propagation velocity, i.e., the average velocity at which the luminous flame front travels throughout the combustion tube, was one of the measurements used to evaluate combustion enhancement. These velocities were compared under light and no light conditions for otherwise identical conditions. The light source was

the continuous EIMAC, irradiating always from the left hand side of the combustion chamber. The spark igniter was discharged from the right hand side or the left hand side causing the flame to propagate toward or away from the light source, respectively.

Previous[1] enhancement experiments measuring the average flame propagation velocity were carried out only with the flame propagating toward the light source. The increase in velocity was found to be small at lean mixtures and became more substantial at stoichiometric and rich mixtures (up to 15-20%) at atmospheric pressure. At subatmospheric pressure, enhancement of 10% was obtained at equivalence ratio of unity, and it decreased at lean and rich mixtures to only 2-3%.

Other measurements[4] used to evaluate combustion enhancement for marginal flames (near the lean flammability limit) were extinction distance and extinction time. The former is the propagation distance of the flame along the tube until extinction, and the latter is the time recorded from ignition until extinction. The experiments were conducted with the flame moving away from the light source. It was found that the extinction time and extinction distance are photochemically enhanced, especially for marginal flames. For example, at equivalence ratio of 0.8, the former is increased up to 80% and the latter is increased by 15-25%. No enhancement was detected when the ORC continuous light sources was used.

These preliminary experiments indicated serious difficulties in determining accurate enhancement results. The difficulties were mainly associated with distortion of the flame front, caused by buoyancy effects, and the high luminosity of the light source. The intense light from the source often obscured the flame front and caused uncertainty as to its exact location. The direction of the flame propagating toward or away from the light source might have also been important because of different optical

paths in each case. In the former case (toward), the light absorbing species in the optical path are reactants while in the latter case (away) they are combustion products.

Based on the experience gained during the earlier enhancement work, new experiments were designed. The objective was first to reproduce some of the preliminary enhancement results and then to investigate the effects of equivalence ratio, pressure, and optical path on the level of combustion enhancement achieved. Therefore, similar combustion conditions were attempted. Since the previous light source cracked, a new xenon lamp was purchased from EIMAC, with the same specifications as the previous one. As before, the lamp operated at 500 watts and the combustible mixture was propane/air.

In the new tests, the emphasis was on measuring flame propagation velocity to evaluate combustion enhancement. Thus, no extinction distances or extinction times were recorded. However, the scope of the work was broadened to include two different optical paths between the flame front and the light source. The first path contained reactants and it was designated as right hand side (RHS - because the flame was traveling toward the lamp, from right to left), and it was similar to the earlier work. Conversely, the new path contained products, and it was designated as left hand side (LHS - because the flame was moving away from the lamps, from left to right). In order to maximize the accuracy of the enhancement data and to minimize the effects of any other combustion variables, the combustion conditions for any two consecutive runs were kept constant with the exception of the light source being either on or off. Usually, the first run was without radiative enhancement (dark-light off), and the second run with enhancement (light on).

These new experimental work consisted on a matrix of 20 tests; 5 equivalence ratios, 2 pressures and 2 optical paths. Each test was conducted at least twice, (dark and light) resulting in a total of over 40 runs, summarized in Table I. The equivalence ratio ranged from fuel lean .79 and .85, to stoichiometric 1.0, and then to fuel rich; 1.19 and 1.50. The two pressures were 1 atmosphere and 400 torr. The two optical paths (RHS & LHS) and the dark and light conditions were described above.

Due to the fact that the combustor was made of a relative short quartz tube and sealed on both ends, the flame propagation velocity throughout it was not constant. In order to improve comparison between enhanced (light) and non-enhanced (dark) runs the tube was divided into three sections; left, middle and right, and for each section the flame velocity was measured and designated as v_1, v_m, and v_r, respectively. The velocity measured at the section closest to the VUV light source, namely v_1, is probably most indicative of any enhancement effect, and therefore only it was used for determining whether combustion enhancement occurred or not. For the sake of completeness the velocities at the other two sections were also measured. However, they were not used for evaluation of enhancement because most, if not all, the VUV radiation was probably absorbed at the left section of the combustion tube.

Table I summarizes all the experimental results. In general, as expected, the flame accelerates from ignition, reaches its maximum velocity at the middle section of the tube, and then decelerates as it approaches the sealed end. Maximum velocities are obtained at equivalence ratios of 1.0 and 1.2, which is consistent with reported burning velocities for propane-air mixtures[2]. However, our measured maximum velocities are almost one order of magnitude higher than the 40 cm/s max. reported in the

Table I - Flame Propagation Velocities

Run #	Equivalence Ratio	Pressure 1 atm/ 400 torr	Optical Path LHS→ RHS←	Dark/ Light	Flame Propagation Velocities cm/s			Comments Enhancement/ Inhibition/ same
					v_l	v_m	v_r	
1	.79	1 atm	LHS→	D	216.7?	156.2	69.7	
2	.79	1 atm	"	L	136.4	121.4	67.8	substantial
3	.79	1 atm	"	L	94.8	108.4	73.8	inhibition
4	.79	400 torr	"	D	89.4	123.5	88.5	
5	.79	400 torr	"	L	108.4	128.6	74.3	enhancement
6	.79	1 atm	←RHS	D	75.9	111.4	84.0	
7	.79	1 atm	"	L	68.6	105.3	83.1	inhibition
8	.79	400 torr	"	D	80.5	117.0	98.4	
9	.79	400 torr	"	L	89.1	---	--	enhancement
10	.85	1 atm	LHS→	D	106.6	154.4	100.4	
11	.85	1 atm	"	L	---	---	81.9	-----
12	.85	400 torr	"	D	224.0	151.7	113.4	
13	.85	400 torr	"	L	256.5	193.9	104.8	enhancement
14	.85	400 torr	"	L	---	169.8	115.6	
15	.85	1 atm	←RHS	D	102.4	149.9	103.6	
16	.85	1 atm	"	L	101.1	128.2	90.3	same
17	.85	400 torr	"	D	106.9	158.0	115.6	
18	.85	400 torr	"	L	102.4	156.2	115.6	same
19	1.0	1 atm	LHS→	D	---	216.7	184.2	
20	1.0	1 atm	"	L	---	---	111.3	
21	1.0	400 torr	"	D	---	221.6	184.2	
22	1.0	400 torr	"	L	---	---	---	light too intense, location of flame front obscured
23	1.0	1 atm	←RHS	D	142.1	205.9	---	
24	1.0	1 atm	"	L	---	---	---	
25	1.0	400 torr	"	D	184.2	250.5	---	
26	1.0	400 torr	"	L	---	---	---	

Table I - Flame Propagation Velocities (Cont'd)

Run #	Equivalence Ratio	Pressure 1 atm/ 400 torr	Optical Path LHS→ ←RHS	Dark/ Light	Flame Propagation Velocities cm/s			Comments Enhancement/ Inhibition/ same
					v_l	v_m	v_r	
27	1.19	1 atm	LHS→	D	---	355.8	307.1	
28	1.19	1 atm	"	L	---	---	236.6	
29	1.19	400 torr	"	D	---	265.5	231.2	
30	1.19	400 torr	"	L	---	---	182.4	light too intense,
31	1.19	1 atm	←RHS	D	202.3	301.6	---	flame front
32	1.19	1 atm	"	L	---	---	---	obscured
33	1.19	400 torr	"	D	225.8	308.9	---	
34	1.19	400 torr	"	L	---	---	---	
35	1.50	1 atm	LHS→	D	75.9	187.8	112.0	substantial
36	1.50	1 atm	"	L	160.8	174.3	93.9	enhancement
37	1.50	400 torr	"	D	77.7	168.9	119.2	
38	1.50	400 torr	"	L	---	151.7	110.2	-----
39	1.50	1 atm	←RHS	D	114.9	158.0	106.6	
40	1.50	1 atm	"	L	121.0	205.9	144.5	enhancement
41	1.50	400 torr	"	D	108.4	---	---	
42	1.50	400 torr	"	L	110.2	---	---	same

literature for laminar flames. This can be easily explained by turbulence generated by the flow, induced due to the thermal expansion of the gas in the confined tube. Turbulence produces wrinkling of the flame surface. The resulting increase of surface increases the rate of burning. This in turn, produces more turbulence and hence increased wrinkling so that the flame front becomes nonsteady and self-accelerating. Therefore, our measured velocities seemed to be reasonable and thus acceptable. Because of these high burning velocities at equivalence ratio of 1.0 to 1.2 resulting in high intensity and obscurity of the flame front, no velocity measurements were available near the lamp (v_1). At the other equivalence ratios, leaner (.79 and .85) as well as richer (1.5), velocity measurements were taken. Comparison of these measured flame velocities at the tube section near the light source with and without the VUV radiation and under otherwise identical conditions, reveals some level of enhancement. However, the results are not quite conclusive. This is so because of two cases in which inhibition rather than enhancement was observed, and because of three other cases in which neither enhancement nor inhibition was observed.

It is interesting to note that the inhibition occurred at fuel-lean conditions and atmospheric pressure, but when the pressure was reduced to 400 torr enhancement took over. The data are too limited to attempt to fully explain it. However, this pressure-dependent inhibition probably indicates the increasing importance of some three-body radical recombination reactions. It is also worth noting that more enhancement was observed when the flame was traveling from left to right. A reasonable explanation for this observation is that in this case the VUV radiation is available right at ignition time (relatively low temperature) when oxygen atoms are really needed to support the combustion wave via chain branching. In all the cases

where the flame was propagating toward the light source (RHS) either slight increases or no changes in velocities where detected, indicating probably that once the flame is propagating, it thermally produces adequate concentration of radicals and there is no need for additional photochemically generated radicals.

To sum it up, enhancement was observed during the inception stages of the flame at fuel-lean and fuel-rich conditions. No data was obtained at near stoichiometric conditions, and some inhibition was detected at very lean conditions and atmospheric pressures. Although a considerable effort was made and a large number of runs was conducted, the data obtained are still scarce due to experimental difficulties outlined above. Nevertheless, the data seem to be somewhat supportive, though not quite confirmative, of the radiative enhancement concept. Analytical modeling was then invoked to better understand and interpret the experimental data as described in the next section, in an attempt to resolve conclusively the question whether radiative augmented combustion works or not.

2. Analytical Modeling

Initiation: The analytical model for combustion initiation has been discussed in a previous paper.[6] A term accounting for heat loss to the surroundings has been added to allow a more detailed examination of the effect of heat loss on initiation. The heat loss has been taken proportional to the difference between gas and ambient temperatures, with heat loss coefficient calculated from $h_c = 16 \kappa / \rho \, C_\rho \, d^2$; κ = thermal conductivity. The diameter, d, used is that estimated for the ignition kernel, based on the irradiated cross-sectional area.

In a modeling effort complementary to the ignition experiments with argon fluoride (ArF) and fluorine (F_2) excimer lasers; model inputs corresponding to these experiments were determined. Specifically, fluences

and heat loss coefficients were calculated from the estimated irradiated cross-sectional area and measured energy outputs from the lasers. Critically damped pulse shapes were determined to give resulting pulse widths (full width, half maximum) equivalent to those typical for the two lasers (6 ns for F_2, 10 ns for ArF). The numerical predictions obtained indicated that at currently available fluences, shown as dotted lines in Figure 4, the shorter wavelength laser (F_2) is capable of achieving photochemical ignitions, while the ArF laser should not be. The bars drawn in this figure indicate the minimum fluence predicted to ignite by photochemical means a premixed hydrogen-oxygen mixture at an equivalence ratio of 0.6 and at 20 kPa for the wavelengths of the F_2 (157 nm) and ArF (193 nm) lasers. These values were calculated from the radiative ignition model by increasing the value for the fluence (i.e., irradiance, as the pulse width remains the same) until a solution indicating ignition was obtained. The resulting fluences are 36 and 2.7×10^5 mJ/cm^2, respectively. This significant difference in fluences (and therefore energies) is primarily due to the spectral selectivity of the absorption coefficient[7] of the oxygen molecule. At 157 nm, which is in the Schumann-Runge continuum, the absorption coefficient is 167 cm^{-1}, and at 193 nm, which is in the S-R bands, it is 0.027 cm^{-1}, about four orders of magnitude lower. A secondary effect is indicated by comparison of the net absorbed energy (proportional to fluence times absorption coefficient) for these two wavelengths which reveals the F_2 laser is igniting with somewhat lower (83%) energy. Modeling results suggest that this effect is due to the production of O(^{1}D) at the lower wavelength. Namely, when the same calculations are performed using for O(^{1}D) reactions the rate constants for the analogous reactions of the ground state, the difference in absorbed energy requirements disappears. Although the picture is complicated, we suggest that the beneficial effect of O(^{1}D) is due to its great reactivity
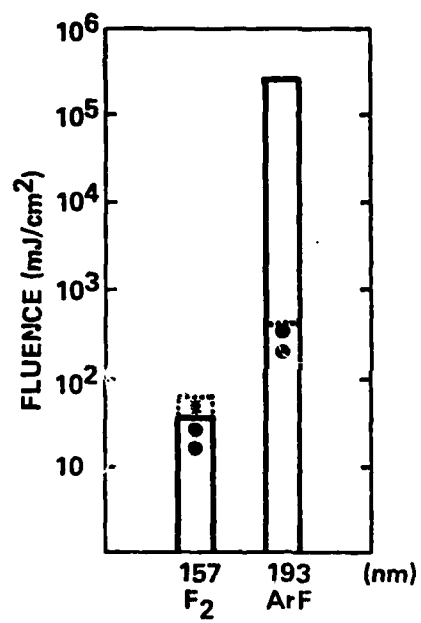
Figure 4. Comparison of fluorine and argon-fluoride laser as igniters;
* = ignition, ● = no ignition; bars represent predicted fluence
for H_2/O_2, ϕ 0.6, 20 kPa, and dotted lines represent available
fluence for experiments.

producing more rapid thermalization, resulting in more efficient utilization of the remaining pool of fast radicals. Experimental results indicated by the symbols for ignition and no-ignition events agree with these predictions. Although the fluence of the F_2 laser is considerably smaller than that of the ArF laser, it successfully achieved ignition, while the ArF failed in photochemically igniting the same gaseous mixtures.

Minimum ignition energies for combustible gaseous mixtures are typically given as a function of equivalence ratios at various pressures. Since it was very difficult in our experiments to vary accurately the energy emitted by the laser and absorbed by the mixture, we chose to keep it constant and instead vary the pressure of the mixture. Figure 5 depicts the minimum pressure at which the mixture is photochemically ignitable by the F_2 laser versus equivalence ratio for hydrogen-oxygen and hydrogen-air mixtures. The curves in the figure are derived from analytical predictions for minimum ignition pressures. The only model input which was varied was the value used for the heat loss coefficient which was changed only according to its pressure dependence. A search was performed until two pressures were obtained which differed by 1 kPa, with ignition indicated for the higher and not for the lower. For H_2/O_2 and equivalence ratio of 0.6, such solution curves are displayed on the phase plane in Figure 6. It is interesting to observe the expected cusp-like behavior in the neighborhood of the saddle point. This procedure was carried out for a sufficient number of equivalence ratios to allow the curves to be drawn accurately.

The experimental results in Figure 5 are indicated with bars to represent the uncertainty in the results obtained due to fluctuations in laser output. The agreement between analytical predictions represented by the solid lines and experimental results shown as data points is very satisfactory. As expected, the results show that it is easier to ignite
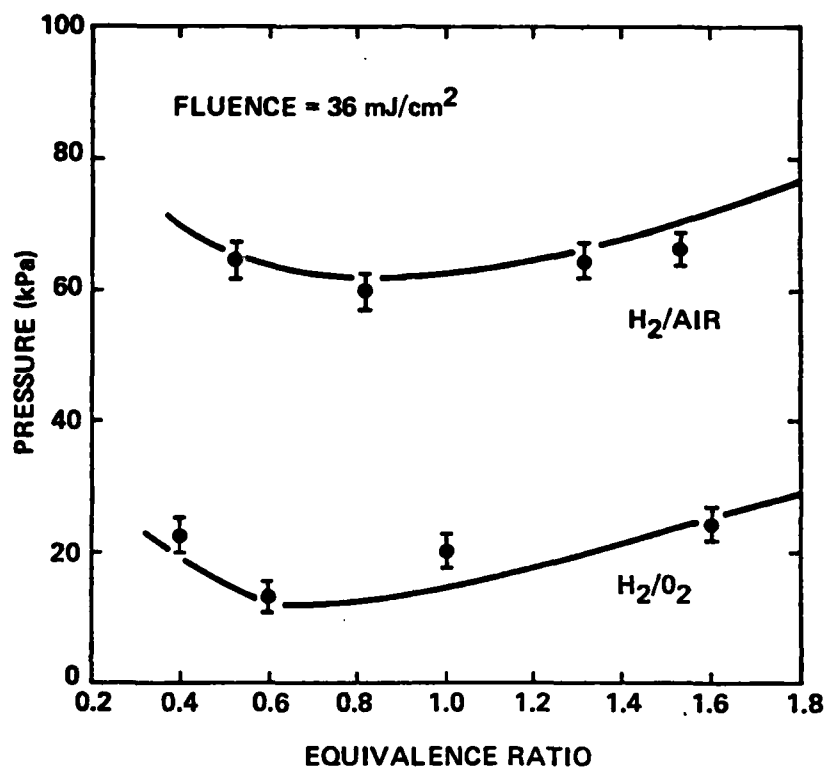
Figure 5. Minimum ignition pressure for H_2/O_2 and $H_2/$mixtures with F_2 laser; comparison of theoretical curves with experimental data.
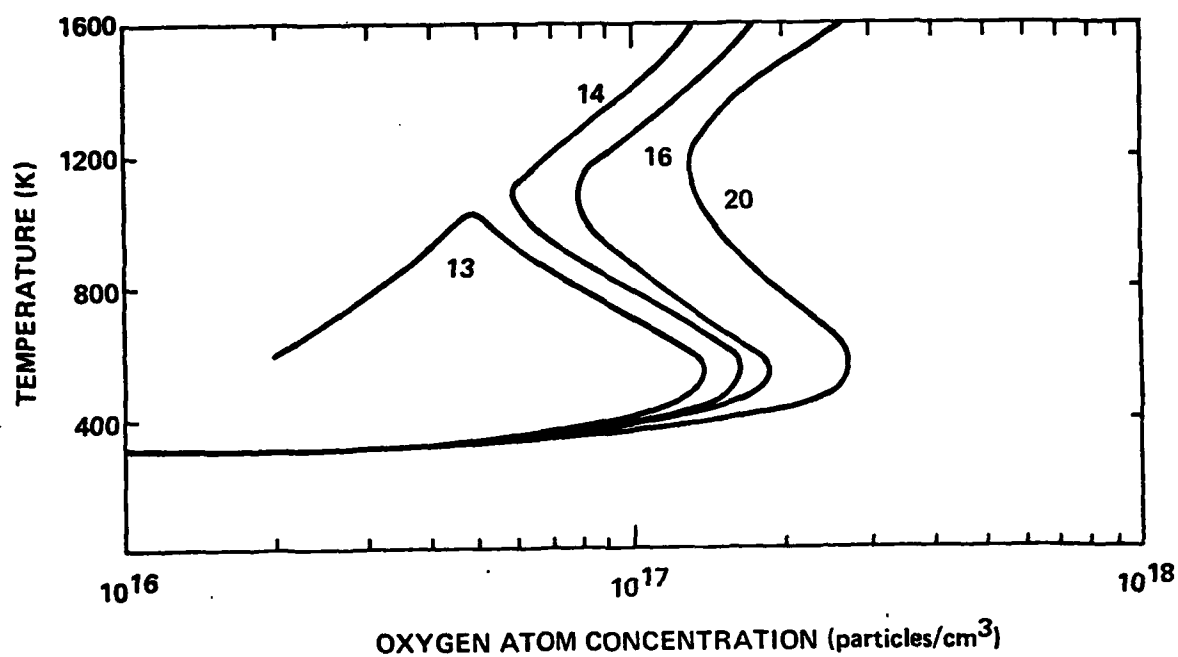
Figure 6. Solution curves for the determination of minimum ignition pressure with fluorine laser; hydrogen-oxygen at equivalence ratio of 0.6; numbers by curves are pressures (kPa).

H_2/O_2 than H_2/air mixtures. The primary reason for the increase in pressure needed for the air system to ignite is the necessity to increase molecular oxygen concentration so as to achieve the required production of oxygen atoms upon irradiation. Indeed, the critical O_2 concentration somewhat exceeds that for the corresponding H_2/O_2 mixture due to the presence of the diluent, N_2, resulting in an increase in thermal inertial, and to the deleterious effects of increased pressure, e.g., increased rates for certain chain termination paths. Also, it is important to note that experimental and numerical results indicate that fuel-lean mixtures with some excess oxygen are more favorable for photochemical ignitions than other mixtures, with the most favorable mixture at an equivalence ratio of around 0.6. This finding is quite different from that for spark ignition in which minimum ignition is found to occur at about equivalence ratio of unity. Again, the explanation is that increased molecular oxygen results in higher atomic oxygen concentration. However, when equivalence ratio is further reduced, the rate of chemical heat release is decreased due to the lessened availability of fuel molecules, which necessitates higher minimum pressure for ignition.

Enhancement: An effort was made to investigate combustion enhancement using a numerical model which allows prediction of laminar flame properties. A computer program developed by Lund[8] at Lawrence Livermore Lab. was employed. The formulation of the model describing the propagation of a one-dimensional, planar, premixed laminar flame, is summarized briefly here. The governing equations include balances for each chemical species (incorporating individual molecular diffusion coefficients, proportional to $T^{1/2}/\rho$), the equation of continuity (obtained by summing the balances over all species and thus imposing a constraint on the diffusion coefficients), and equations of momentum and energy conservation. Detailed chemical kinetics are included; for

methane-air flames, 26 chemical species and 78 chemical reactions with forward and reverse rates are considered. Finite difference equations are derived and solved implicitly in time by a generalized Newtonian iteration procedure on a grid which is dynamically rezoned to concentrate zoning at the flame front. The imposition of appropriate boundary conditions allows the simulation of both confined (enclosed chamber) and unconfined (open-ended chamber) flames. For the confined case, the volume is held constant resulting in increasing pressure as the flame progresses; while for unconfined flames, the pressure remains constant. The implementation described by Lund was used in this study. C. K. Westbrook prepared the computer inputs, executed the program and assisted us in interpreting the results.

The basic approach used to simulate the irradiation of the unburned fuel/air mixture was to modify the forward and reverse rates for the reaction

$$O_2 \rightleftarrows O + O$$
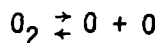
in order to increase the quasi-steady state concentration of oxygen atoms in the unburned gas and to leave unchanged the effect of this reaction near the flame front and in the burned gas. Indeed, it was found possible to alter these rates to give composition and temperature of the burned gas the same as those obtained for cases in which the rates were those usually employed. This technique was chosen primarily for its ease of implementation within the existing computer program and its input structure. The pursuit of more conceptually straight-forward approaches, which also allow the spatial and temporal variation of the photodissociation of oxygen molecules and include the photodissociation of all absorbing species is desirable.

The procedure employed to predict laminar flame speed was that described by Westbrook and Dryer[9], and it is summarized briefly here. Initial profiles are guessed for concentrations, velocity, and temperature through the flame. With these initial profiles, the program is then used to compute the temporal and spatial evolution of the flame. In principle, one expects to see the computed flame obtain quasi-steady behavior from which laminar flame properties can be determined. Several attempts at this procedure proved unsuccessful. First, considerable care had to be taken in order to preserve flame and post-flame properties with the new reaction rates for $O_2 \rightleftarrows O + O$. It remains possible that the treatment is not fully adequate, especially in the critical induction region. Second, the concentration of atomic oxygen in the unburned gas was set sufficiently high that the induced reactions resulted in considerably increased tem- perature (e.g. 300 K, initially, increased to $\sim$ 400 K) and, consequently, expansion of the unburned gas in the unconfined case, or increased pressure for the confined case. In fact, this problem persisted throughout the study. For the unconfined flame simulation, the resulting expansion ahead of the flame made computation of laminar flame speeds relative to the unburned gas virtually impossible with the present code. Another problem which results is that the atomic oxygen combines with the fuel species (methane for most of the runs) and produces a variety of oxygenated species, such as formaldehyde and methanol, in front of the flame. In one instance, as much as 10% of the methane was converted to these species in the unburned gas. Clearly, this change in the unburned mixture can strikingly change laminar flame properties, especially for marginal flames.

Among the cases which were run, one approach appeared to circum- vent to some degree several of these problems. The mixture was taken to be methane/air at an equivalence ratio of 0.6 (lean) in an enclosed chamber

(confined). The initial temperature was 300 K and pressure, 101.3 kPa.
A base case was run in which all reaction rates were those normally used
for prediction of methane/air laminar flame properties, with which the
computer program has shown good agreement with experimental data. As dis-
cussed above, the rates for $O_2 \rightleftarrows O + O$ were then altered to preserve
flame and post-flame influence of this reaction, while increasing oxygen
atom concentration in front of the flame to a mole fraction of $\sim 4.5 \times 10^5$
versus $\sim 6.2 \times 10^{-13}$ for the base case. At the same time, in an attempt
to simulate a physical system in which the unburned fuel/air mixture is
irradiated only a short distance ahead of the flame front and not throughout
its entire extent, certain radical recombinations reactions were nearly
turned off at low temperature. The goal of this approach was to prevent
the conversion of methane ahead of the flame and the accompanying increase
of energy deposition, increase in temperature of the unburned gas, and
back pressure on the flame. It must be said that this approach was only
moderately successful in accomplishing these goals. At the same time and
position, the temperature of the unburned gas had risen to 345 K in front
of the flame for the base case and to 383 K in the enhanced oxygen atom
case. Moreover, for the latter approximately 4% of the methane had been
converted to other species.

In the light of these difficulties in comparing laminar flame
speed calculations for the two cases, we present the results in Table II.
Identical profiles were used to start the calculations. It can be seen
that as the flame progresses, its speed is decreasing in both cases, but
at a greater rate in the presence of the increased oxygen atom concentration.
The reasons for this result are not easy to discover, due in part to the
edit facilities of the computer program. No obvious difference in the
reactions in the induction and flame zones have been observed. It remains
to be determined whether the reasons already discussed are chiefly responsible

Table II

Flame Speed Calculation for Methane/air in an enclosed Chamber at Equivalence Ratio of 0.6, initial temperature of 300°K and Initial Pressure of 101.3 kPa.

Normal $O_2 \rightleftarrows O + O$

Enhanced $O_2 \rightleftarrows O + O$

Time (ms)	Position* (cm)	Flame Speed (cm/s)		Time (ms)	Position* (cm)	Flame Speed (cm/s)
80.3	6.01	45.8		80.6	5.90	45.5
90.3	6.46	44.5		89.8	6.30	39.8
98.9	6.83	40.3		99.0	6.62	29.7

*Initial position not equal to zero.

for the differences in flame speed behavior or whether mechanisms not yet
discerned are the cause.

The use of a numerical model for prediction of laminar flame
properties appears to have the potential for giving valuable guidance and
insight into the underlying processes. Our efforts to date have neither
realized this potential nor established the validity of the simulation
procedure employed. In the future, it appears desirable to examine further
the cases which have been run and to run additional cases in which a
more direct comparison of results simulating irradiated and unirradiated
conditions can be made.

REFERENCES

1. Lavid, M., "Radiation/Catalytic Augmented Combustion," Final Technical Report AFOSR-TR-82-0132, July, 1981.

2. Lewis, B. and VonElbe, G.: <u>Combustion, Flames and Explosion of Gases</u> 2nd Ed., Academic Press, 1967.

3. Eckbreth, A. C., Combustion Fundamentals, Section IV, pp. 13, 10-10, Exxon Series, 1981.

4. Lavid, M.: "Radiation/Catalytic Augmented Combustion." Third Interim Report, Technical AFOSR-TR-81-0287, September, 1980.

5. Lee, J. H., Kngstautas, R., and Yoshikawa, N.: Photochemical Initiation of Gaseous Detonations, Acta Astronautica, 5, 971, (1978).

6. Cerkanowicz, A. E. and Stevens, J. G.: Case Studies in the Simulation of Novel Combustion Techniques, Proc. of the 1979 Summer Computer Simulation Conference, p. 170, July, 1979.

7. Okabe, H.: <u>Photo-Chemistry of Small Molecules</u>, John Wiley and Sons, 1978.

8. Lund, C., HCT - A general computer program for calculating time dependent phenomena involving one-dimensional hydrodynamics, transport, and detailed kinetics, Report UCRL-52504, Univ. California, Lawrence Livermore Lab., August, 1978.

9. Westbrook, C. K. and Dryer, F. L., "Prediction of Laminar Flame Properties of Methanol - Air Mixtures," Combustion and Flame, 37, pp. 171 - 192, 1980.

PROFESSIONAL PERSONNEL
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Dr. J. G. Stevens - Analytical Consultant - PhD Courant Institute of

Mathematic Sciences, New York University, 1972.

INTERACTIONS/OUTSIDE INTEREST

A. Talks and Papers

Four internal (Exxon) presentations on the program were made to management and professionals on April 2, July 23, September 14, and November 5, 1981.

A paper entitled "Photochemical Ignition of Gaseous Mixtures" was presented at the Eastern States Section Combustion Institute meeting on Chemical and Physical Processes in Combustion on October 27-28, 1981 in Pittsburgh, Pennsylvania (Attachment I).

A presentation was also made at the last AFOSR Contractor's Meeting on "Air Breathing Combustion Dynamics and Kinetics," in Clearwater, Florida, November 16-20, 1981. The presentation was entitled "Radiative and Catalytic Augmented Combustion."

Another presentation on "Radiative Augmented Combustion - Theory and Results" was given at Los Alamos National Lab., Photochemical Division on August 5, 1981.

B. Interest Expressed by Other Scientists

Although a strong interest is expressed in our combustion augmented program, as can be seen by the many requests for additional technical information listed below, it seems that the only ongoing active work that is directly related to our radiative approach is the plasma jet work of Professor Felix Weinberg at Imperial College, London. Prof. Weinberg has carried out experiments and has reported encouraging combustion augmentation results by using chemical and fluid mechanical effects via his novel design of a plasma jet. The kinetics is modified by a supply of radicals from the plasma (especailly H atoms) while the fluid mechanics is modified by the high velocity jet. The plasma jet demonstrated ignition of sub-lean

mixtures, increased flame speeds and conversion rates. The current design
is using a pulsed plasma jet, and there may be a need for developing a
continuous plasma jet plug. Open communication has been established with
Prof. Weinberg and he has been retained as a consultant to Exxon Research
and Engineering and this program.

In the catalytic work, contact has been made with Dr. W. B.
Retallick who has become a consulting engineer after being for several
years a Vice President for R&D at Oxy Catalyst. Dr. Retallick has a
strong interest in the development of the catalytic combustion and believes
that it can be utilized in a partial combustion mode, resulting in lower
catalyst temperatures. Dr. Retallick has been retained as a consultant
and he will provide the catalyst for the prototype flameholder.

During this reporting the following professionals expressed
interest and/or requested additional technical information:

Dr. Nicole Beaudet, PRB - Service Recherche, Bruxelles, Belgique.

Dr. Kenneth Brezinsky, Princeton University, New Jersey.

Professor Eli K. Dabora, University of Connecticut, Storrs, Connecticut.

Dr. F. E. Fendell, TRW, Redondo Beach, California.

Professor Irvin Glassman, Princeton University, New Jersey.

Dr. Alan Hartford, Los Alamos Scientific Lab, New Mexico.

Dr. Robert Hickling, GM Research Laboratories, Engineering Mechanics
Dept., Warren, Michigan.

Dr. Lyle O. Hoppie, Eaton Corporation, Southfield, Michigan.

Professor J. P. Longwell, MIT, Cambridge, Massachusettes.

Dr. W. B. Retallick, Consultant, West Chester, Pennsylvania.

Dr. R. K. Sander, Los Alamos Scientific Lab, New Mexico.

Dr. Tom Sloane, GM Research Laboratories, Physical-Chemistry Dept.
Warren, Michigan.

Dr. Barry R. Taylor, MIT, Cambridge, Massachusettes.

Professor Felix Weinbert, Imperial College, London, England.

Dr. Charles K. Westbrook, Lawrence Livermore Lab, University of California.

Professor Ben T. Zinn, Georgia Institute of Technology, Altanta, Georgia.

SUMMARY: POTENTIAL APPLICATION OF RESEARCH RESULTS

Both the radiative and catalytic techniques have demonstrated the capability to enhance combustion processes and to broaden normally encountered stability limits.

The work on radiative ignition and combustion enhancement is providing fundamental information on a unique combustion process. Concepts which represent a new departure and extension of conventional combustion practice can evolve from the experimental data being obtained. Aspects of the radiative ignition and enhancement concept have been demonstrated in our laboratory under static (no flow) conditions. Successful pulsed light source ignition experiments reconfirm the radiative augmented concept and demonstrate the technical feasibility of designing an advanced optical-radiative igniter. Reproducible ignitions with a continuous light source imply the possibility of using the light as an optical radiative flame stabilizer with no pressure loss instead of the conventional intrusive flameholders. Encouraging results of combustion enhancement in terms of higher flame propagation velocities and larger extinction times and distances suggest a potential to extend the combustor operating limits utilizing the radiative technique. It is construed that the enhanced flame propagation can be translated into higher combustion rate and extended flammability limits.

From the experimental results reported here we gain confidence that radiative augmented combustion is a potentially viable technique to extend current aircraft operating limits. Eventual application to gas turbine engine systems is envisioned both for improved combustor operation and flame holding. Some future areas of potential application are: High altitude combustor reignition following flame-out, drag-free flame stabilization in supersonic combustors, and added flexibility for

conventional combustors to use future alternate fuels. To this end, radiative ignition and combustion enhancement experiments under flow conditions are required as well as continued VUV light source development in the direction of improved beam optics.

The catalytic flame stabilization concept is particularly important to aeropropulsion combustion: turbo propulsion mainburners, afterburners, duct burners and ramjet dump combustors. Potential benefits include improved ignitability, stability as well as efficiency, and combustion design flexibility for alternate fuel usage. In the afterburner application, the conventional bluff-body flameholder can be replaced by a porous catalytic device resulting in less pressure drop than a solid flameholder of equal cross-sectional area. It can broaden its stability range by allowing for operation at inlet velocities, temperatures and fuel mixtures where conventional flameholders begin to fail. In addition, it may have the advantage of being a passive autoignition device.

Finally, an opportunity may exist for the development of an advanced combustor featuring the combined performance of catalytic stabilization and radiative enhanced combustion.

Attachment I

Photochemical Ignition of Gaseous Mixtures

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Photochemical Ignition of Gaseous Mixtures

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Introduction

Operation of systems containing combustion processes is generally
limited by combustion associated phenomena such as flammability, flame
propagation, ignition and stable combustion and by the formation of combustion
related pollutants. Recent research has identified photochemical augmented
combustion as a potentially promising technique for rectifying some of these
limitations. This technique is being researched at Exxon's Corporate Labora-
tories, as part of an Air Force sponsored program[1]. The main objective is
to investigate radiative ignition and enhancement of combustion in unsensitized
fuel-air mixtures via photodissociation of oxygen molecules and of combustion
intermediary species. Currently, pulsed and continuous vacuum ultraviolet (VUV)
and ultraviolet (UV) radiation from various Xenon lamps and Excimer lasers are
being used.

Radiative Ignition Principle

The radiative work has been divided into ignition and enhancement.
However, this paper does not address combustion enhancement and focuses only on
radiative ignition. It presents recent experimental results on the ignition of
various stationary gaseous mixtures by photochemical means. It is postulated
that in radiative ignitions the mechanism follows a photochemical path (vs. a
thermal path) wherein the critical intermediary species are oxygen atoms. These
atoms are produced by photodissociation of oxygen molecules via radiant energy
absorption below 245 nm.

$$O_2 + h\nu \rightarrow O+O$$

However, the most efficient photodissociative production of atomic oxygen
occurs primarily at wavelength below 180 nm, where one of the atoms produced
is in an excited electronic state. When a critical concentration of oxygen
atoms (on the order of 10^{14} atoms/cm^3[2]) is achieved at any point in the
reactant mixture, combustion initiation occurs. Subsequent reaction of the
atomic oxygen with fuel molecules, as well as other combustion species leads
to ignition and sustained combustion via chain reaction. For example,

$$O + RH \rightarrow OH + R$$

The photochemical enhancement mechanism also depends on production
of oxygen atoms. However, at substantially lower concentration (10^7-10^{14} atoms/
cm^3). The radiative enhancement results were reported elsewhere[3].

Experimental Apparatus

The experimental apparatus, depicted schematically in Fig. 1, provides
the capability of studying the interaction of vacuum ultraviolet and ultra-
violet radiation with gaseous fuel-air mixtures at atmospheric and subatmospheric
pressures, and at room temperature. A quartz cylindrical combustion chamber
2.5 cm diameter and 30 cm long can be irradiated end-on by light sources of
various types. An adjustable length cell is used between the combustion

chamber and the light source in order to provide a diagnostic procedure to evaluate radiation optics and absorption effects. The cell is evacuated or filled to various pressures with air, oxygen, or nitrogen. Current light source capability includes three high pressure Xenon or mercury-Xenon plasma arcs optimized for different wavelength regions and two Excimer lasers, as follows:

(1) ILC - A pulsed Xenon point source with a sapphire window is used to provide radiation in the 140-200 nm spectral region. Energy input is 0.5 to 50J.

(2) ORC - A continuous mercury-Xenon source with quartz optics provides up to 1 kW of energy and operates in the 200-400 nm spectral region.

(3) EIMAC - A continuous Xenon point source is used in combination with a UV grade sapphire window and an elliptical reflector (sealed in the arc chamber) to provide a focused source of radiation in the 150-400 nm spectral region. This source can be operated in the continuous mode at a power level up to 500 W, and has also been used in the pulsed mode at energy levels of up to 50J.

(4) Lumonics TE 861, ArF Excimer laser at wavelength of 193 nm. Average pulse energy is about 50mJ. Focused beam cross section is 1.5 mm x 12 mm and measured average fluence is 350mJ/cm2.

(5) Lumonics TE 861, F2 Excimer laser at wavelength of 157 nm. Average pulse energy is about 10mJ. Focused beam cross section is 1 mm x 3 mm, and measured average fluence is 30 mJ/cm2.

Ignition Results and Discussion

Ignition has been attempted by using a pulsed light source (ILC), a continuous light source (EIMAC) and pulsed lasers (157 and 193 nm).

Various gaseous fuel/air and fuel/oxygen mixtures have been successfully ignited by using only a light source (no thermal effects). A few of the reactive mixtures ignited by the pulsed ILC light source are hydrogen/oxygen, methane/air and propane/air. The experimental variables besides the reacting mixtures were equivalence ratio, combustion chamber pressure and power of the light. The gases were admitted to the combustion chamber at predetermined equivalence ratios and pressures and then the light source was turned on. If the mixture did not ignite the capacitance of the light power supply was increased until by trial and error the critical power for ignition was found.

Figure 2 shows such minimum light ignition energies for a mixture of propane-air as a function of equivalence ratio. All measurements were made at room temperature (about 20°C), under two chamber pressures; 1 atmosphere and 500 torr and with two ILC light sources designated as #3 and #9. A minimum spark ignition energy reproduced from Reference 4 was drawn on the figure for comparison. It is noted that the minimum light ignition energy curves are similar in shape to the spark ignition curve, namely, a

minimum in the ignition energy occurs at some equivalence ratio. Increasing or decreasing the equivalence ratio from the value corresponding to the minima result in an increase in light as well as spark ignition energies until the equivalence ratios are outside the flammability limits and all attempts to ignite fail. It is important to note that light minimum ignition energy occurs at a leaner equivalence ratio than that of spark ignition, and that light minimum ignition energies are less sensitive to pressure variations than spark ignition.

The significance of the successful pulsed light source ignition experiments is two-fold: it reconfirms the above mentioned concept of radiative ignition, and it demonstrates technical achievement in designing an advanced optical radiative igniter.

The EIMAC continuous light source also ignited a stoichiometric mixture of gaseous propane-oxygen at atmospheric pressure and room temperature. Actually, the photochemical ignition caused a detonation wave which shattered the quartz reactor and cracked the lamp. This detonation wave is similar to those reported by Lee et al.[5] which required a minimum value of photodissociative free radicals as well as an adequate gradient of these radicals. This first reported successful ignition with a continuous light source implies the potential of using the light as an optical-radiative flame stabilizer with zero pressure drop instead of the conventional flameholders.

Preliminary experimental laser ignitions were conducted at two wavelengths: 193 nm (ArF), and 157 nm (F_2). They corroborated analytical predictions that the fluorine laser is much more capable than the argon-fluoride laser of photochemically igniting various H_2/O_2 and H_2/air mixtures at atmospheric and subatmospheric pressures. For example, in the case of stoichiometric H_2/air mixture at 1 atm, the F_2 laser required a fluence of less than 30 mJ/cm^2 for radiative ignition, while the ArF could not ignite even with a fluence of 350mJ/cm^2. According to analytical computation the ArF laser needed an increase in fluence of one order of magnitude from its currently available level for a successful radiative ignition.

Conclusions

The radiative ignition experimental results reported here demonstrate the opportunity of using radiative augmented combustion as a technique to extend current combustors operating limits. However, before final conclusions can be drawn, ignition and enhancement experiments must be planned for flowing systems. Only after obtaining positive radiative ignition and enhancement results under various flow conditions should this technique be considered as a feasible means for combustion augmentation.

Acknowledgment

References

(1) Lavid, M., "Radiation/Catalytic Augmented Combustion, Final Technical Report AFOSR-TR-81, July 1981.

(2) Cerkanowicz, A. E. and Stevens, J. G., "Case Studies in the Simulation of Novel Combustion Techniques," 1979 Summer Computer Simulation Conference, July 16-18, 1979.

(3) Lavid, M., "Radiation/Catalytic Augmented Combustion," Third Interim Report AFOSR-TR-80, September 1980.

(4) Lewis, B. and VonElbe, G., "Combustion, Flames and Explosion of Gases," 2nd Ed. p. 334, Academic Press, 1967.

(5) Lee, J. H., Knystautas, R., and Yoshikawa, N., "Photochemical Initiation of Gaseous Detonations," Acta Astronautica, Vol. 5, pp. 971-982, 1978.

Figure 1

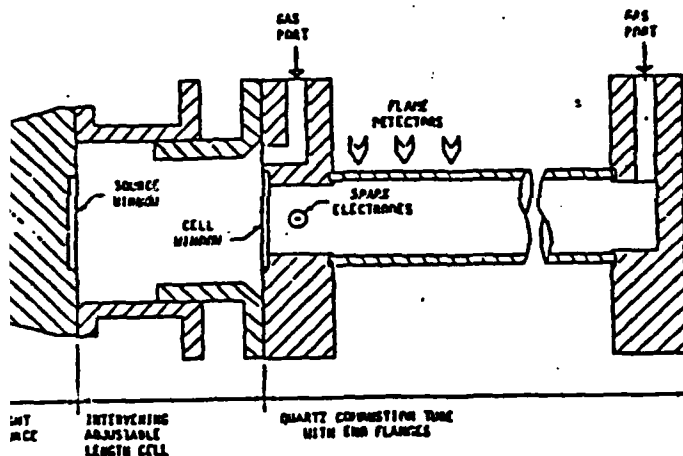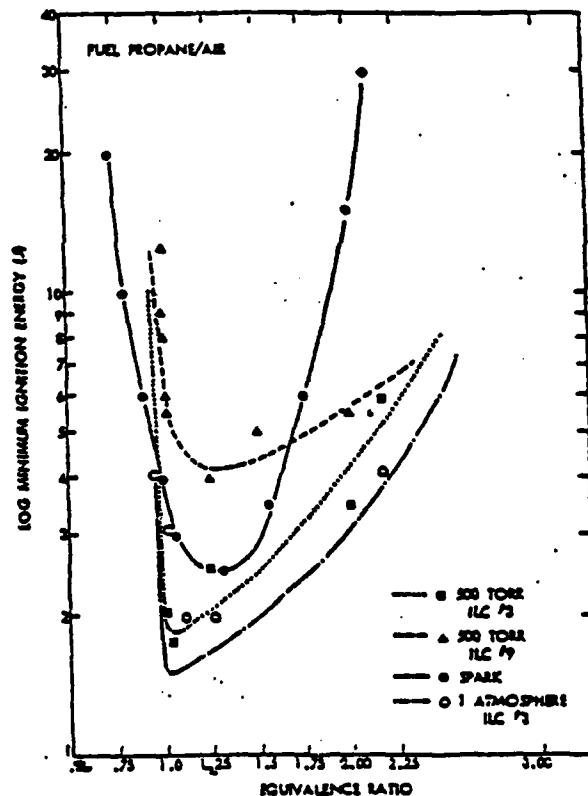Experimental Apparatus

Enhancement Combustion - Schematic

Figure 2

Minimum Spark and Radiative Ignition Energies vs.
Equivalence Ratio at (Sub)Atmospheric Pressure

DATE

TIME